

## PATENT ABSTRACTS OF JAPAN

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## (54) CONTINUOUS PRODUCTION OF NAPHTHALENEDICARBOXYLIC ACID

## (57)Abstract:

PURPOSE: To continuously produce the subject compound by oxidizing dimethylnaphthalene or its oxidized derivative with molecular oxygen in the presence of a catalyst composed of a heavy metal oxidizing catalyst and bromine in a lower fatty carboxylic acid solvent.

CONSTITUTION: Dimethylnaphthalene and/or its oxidized derivative is oxidized with a molecular oxygen-containing gas in the presence of a heavy metal compound composed of Co, Mn and Ce and a bromine compound, preferably an acetate and a bromide as catalysts in a lower fatty carboxylic acid solvent (e.g. acetic acid) at 180 to 230°C. By addition of Ce, it forms chelate complexes selectively with ortho-benzenedicarboxylic acids formed as by-products. The chelate complexes are removed out of the reactional system and the catalysts are recycled while keeping the catalytic activities of Co and Mn. The heavy metal oxidizing catalyst is used in an amount of 0.2 to 0.4wt.% based on the solvent. This naphthalenedicarboxylic acid is useful, e.g. as a polymer material, an intermediate for synthesis of dyes and a raw material for resins.

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## TECHNICAL FIELD

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[Industrial Application] This invention relates to the approach of oxidizing a dimethylnaphthalene and/or its oxidization derivative and manufacturing continuously naphthalene dicarboxylic acid (it being hereafter called NDCA for short). Furthermore, it is related with the oxidation approach which carried out the circulation reuse of the oxidation reaction catalyst in detail.

## EFFECT OF THE INVENTION

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[Effect of the Invention] According to the approach of this invention, NDCA can be manufactured efficiently and continuously on a scale of industrial.

## PRIOR ART

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[Description of the Prior Art] NDCA and its ester (it may be hereafter called NDCA etc. for short) are matter useful as polymeric materials, color intermediate field, etc. Especially the polyethylenenaphthalate formed from 2 and 6-NDCA etc. and ethylene glycol excels polyethylene terephthalate in thermal resistance, breaking strength, etc., and attracts attention as materials, such as a film and a food packaging material. Furthermore, polybutylene naphthalate resin has a large crystallization rate compared with polybutyrene terephthalate resin, and since it has high resistance to moist heat, NDCA etc. is useful also as a resin raw material.

[0003] Conventionally, as the manufacture approach of NDCA, in dialkyl naphthalene and/or its oxidization derivative, cobalt, manganese, a bromine, etc. are used for a catalyst and the approach of oxidizing by molecular oxygen is proposed among the low-grade aliphatic-carboxylic-acid solvent.

[0004] This approach is classified, when it is classified into a batch process, half-continuous system, or continuous system according to that reaction format and does not

consider a catalyst as recovery and the case where a reuse is carried out.

[0005] In order to manufacture NDCA cheaply on a scale of industrial, since equipment effectiveness is low, it is necessary to make it a continuous-running method and to raise equipment effectiveness in the reaction format of a batch process or half-continuous system. Moreover, it is advantageous when carrying out the circulation reuse of the remaining reaction mother liquors which carry out the circulation reuse of the catalyst, namely, collected generation rough NDCA(s) from the reaction mixture, and/or the washing filtrate of generation rough NDCA in order to use a comparatively expensive catalyst generally raises the economical efficiency of a process by manufacture of the carboxylic acid by the liquid phase oxidation of aromatic hydrocarbon.

[0006] As one of the approaches of collecting and carrying out the circulation reuse of the oxidation reaction catalyst from an oxidation reaction mixture, the method of collecting only catalysts from a reaction mixture is proposed. For example, in oxidation reaction of 2 and 6-diisopropyl naphthalene, in case it reacts by making cobalt, manganese, a cerium, and a bromine into a catalyst, in order to collect catalysts from a reaction mother liquor, the approach (publication-number No. 252613 [ two to ] official report) of using the approach (publication-number No. 250850 [ two to ] official report) of using alkali, the approach (publication-number No. 250851 [ two to ] official report) of using a sulfuric acid, a sulfuric acid, and alkali etc. is proposed. However, any approach cannot say that actuality and economical efficiency are enough, in order to manufacture NDCA cheaply on a scale of industrial seen from the field of corrosive [ over the equipment quality of the material ], or operability.

[0007] On the other hand, the approach of carrying out the cyclic use of waste water of the reaction filtrate is proposed as other one approach of collecting and carrying out the circulation reuse of the oxidation reaction catalyst from an oxidation reaction mixture. For example, in oxidation reaction of 2 and 6-diisopropyl naphthalene, in case it react by make cobalt, manganese, a cerium, and a bromine into a catalyst, the approach (publication number No. 330039 [ four to ] official report) of perform a two-step reaction and carry out the cyclic use of waste water of the reaction filtrate be propose, but since this approach have the process of post-oxidation, the initial investment of a process increase and it cannot say that it be advantageous in respect of economical efficiency.

[0008] Furthermore, the approach of carrying out the reuse of the reaction mother liquor is proposed as the oxidation approach of 2 and 6-diisopropyl naphthalene or 2, and 6-diethyl naphthalene (publication-number No. 266846 [ four to ] official report). Although the circulation oxidation reaction by this method is fundamentally possible, if it takes into consideration that a lot of cobalt and manganese still go together into rough NDCA after reaction mother liquor separation in oxidation reaction of 2 and 6-diisopropyl naphthalene or 2 and 6-diethyl naphthalene, it needs to wash rough NDCA with an acetic acid, water, etc., needs to collect these catalysts, and needs to attain reduction-ization of catalyst cost. By the way, reference is not made [ dimethylnaphtalene ] at all about oxidation reaction with the method concerned. And according to examination of this invention persons, in the case of the dimethylnaphtalene, when oxidized by the method concerned, the serious problem that a reaction will stop at the circulation first time occurred.

[0009] When this invention persons study wholeheartedly about this cause, they differ from the case of 2 and 6-diisopropyl naphthalene or 2 and 6-diethyl naphthalene. In the case of a dimethylnaphtalene, the cause which a reaction stops at the circulation first time Orthochromatic-benzene dicarboxylic acid, such as trimellitic acid which is a naphthalene nucleus cleavage by-product, a phthalic acid, and a methylation phthalic acid Since (it may be hereafter called ODCA for short) formed a heavy-metal oxidation catalyst and a stable chelate mold complex and a catalyst was inactivated, it was able to be shown clearly that it is a sake according to the effective amounts of catalysts only by filling up the catalyst accompanied to rough NDCA running short.

[0010] Although a means to use a lot of heavy-metal catalysts as a policy for avoiding these problems can be considered, if in the case of a dimethylnaphtalene (differing from the case of 2 and 6-diisopropyl naphthalene or 2 and 6-diethyl naphthalene) proper catalyst concentration is comparatively low and uses a lot of catalysts for \*\* and others on yield, NDCA yield will fall conversely. In addition, the heavy metal with which generation rough NDCA was added superfluously deteriorates between oxidation reaction, an operation of the catalyst for which the generated oxide deteriorated colors it dark gray, and a very disadvantageous result [ say / that the combustion loss of that

purification becomes very difficult and the low-grade aliphatic carboxylic acid further used as a solvent increases ] is caused.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the approach of oxidizing a dimethylnaphthalene and/or its oxidization derivative and manufacturing continuously naphthalene dicarboxylic acid (it being hereafter called NDCA for short). Furthermore, it is related with the oxidation approach which carried out the circulation reuse of the oxidation reaction catalyst in detail.

[0002]

[Description of the Prior Art] NDCA and its ester (it may be hereafter called NDCA etc. for short) are matter useful as polymeric materials, color intermediate field, etc. Especially the polyethylenenaphthalate formed from 2 and 6-NDCA etc. and ethylene glycol excels polyethylene terephthalate in thermal resistance, breaking strength, etc., and attracts attention as materials, such as a film and a food packaging material. Furthermore, polybutylene naphthalate resin has a large crystallization rate compared with polybutyrene terephthalate resin, and since it has high resistance to moist heat, NDCA etc. is useful also as a resin raw material.

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[0008] Furthermore, the approach of carrying out the reuse of the reaction mother liquor is proposed as the oxidation approach of 2 and 6-diisopropyl naphthalene or 2, and 6-diethyl naphthalene (publication-number No. 266846 [ four to ] official report). Although the circulation oxidation reaction by this method is fundamentally possible, if it takes into consideration that a lot of cobalt and manganese still go together into rough NDCA after reaction mother liquor separation in oxidation reaction of 2 and 6-diisopropyl

naphthalene or 2 and 6-diethyl naphthalene, it needs to wash rough NDCA with an acetic acid, water, etc., needs to collect these catalysts, and needs to attain reduction-ization of catalyst cost. By the way, reference is not made [ dimethylnaphtalene ] at all about oxidation reaction with the method concerned. And according to examination of this invention persons, in the case of the dimethylnaphtalene, when oxidized by the method concerned, the serious problem that a reaction will stop at the circulation first time occurred.

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[0010] Although a means to use a lot of heavy-metal catalysts as a policy for avoiding these problems can be considered, if in the case of a dimethylnaphtalene (differing from the case of 2 and 6-diisopropyl naphthalene or 2 and 6-diethyl naphthalene) proper catalyst concentration is comparatively low and uses a lot of catalysts for \*\* and others on yield, NDCA yield will fall conversely. In addition, the heavy metal with which generation rough NDCA was added superfluously deteriorates between oxidation reaction, an operation of the catalyst for which the generated oxide deteriorated colors it dark gray, and a very disadvantageous result [ say / that the combustion loss of that purification becomes very difficult and the low-grade aliphatic carboxylic acid further used as a solvent increases ] is caused.

[0011]

[Problem(s) to be Solved by the Invention] this invention -- \*\* -- it is in removing alternatively ODCA which faces manufacturing NDCA from a dimethylnaphtalene and/or its oxidization derivative, forms cobalt, manganese, and a complex that a situation [ like ] should be canceled, and inactivates the oxidization activity, and offering the

continuation manufacturing method by oxidization.

[0012]

[Means for Solving the Problem] In the liquid-phase-oxidation reaction of the dimethylnaphtalene which this invention persons inquired wholeheartedly in order to establish the above-mentioned approach, and used heavy metal and a bromine for the catalyst, and/or its oxidation derivative If a cerium is added to cobalt and manganese as a heavy-metal oxidation catalyst at \*\*\*\*\* By forming a chelate mold complex in ODCA and the selection target with which a cerium exists in the system of reaction, and preventing inactivation of the oxidation activity of cobalt and manganese, and depositing as a solid-state, and being accompanied to rough NDCA, it found out that ODCA was removable from a reaction mother liquor, and this invention was completed.

[0013] Namely, this invention uses molecular oxygen content gas for the bottom of existence of the catalyst which consists of a heavy-metal oxidation catalyst and a bromine in a low-grade aliphatic-carboxylic-acid solvent, and a dimethylnaphtalene and/or its oxidation derivative are set to the approach of oxidizing. By facing carrying out the circulation reuse of the catalyst, and adding cobalt, manganese, and a cerium as a heavy-metal oxidation catalyst the activity of cobalt and manganese -- maintaining -- ODCA -- alternative -- the outside of the system of reaction -- removing -- a reaction mother liquor and/or generation -- it is the continuation manufacturing method of NDCA which carries out the whole-quantity circulation reuse of the washing filtrate of a cake, and performs it.

[0014] Hereafter, this invention is explained to a detail.

[0015] The dimethylnaphtalene used as an oxidization raw material by this invention and/or its oxidization derivative could usually be obtained by what kind of approach. Moreover, those mixture is sufficient. As an oxidization derivative, although a formyl naphthoic acid, a methyl naphthoic acid, etc. are mentioned, it is not limited to these at all. And 2 and 6-object is [ among these ] industrially useful especially. An oxidation raw material has the desirable thing of a high grade, and 95% or more of purity, although it is 98% or more preferably, if it is extent which can be removed when extent and oxidation reaction termination happiness-in-the-next-life product which do not affect yield are refined by various approaches, even if isomers, such as components other than 2 and 6-object, 2 [ for example, ], and 7-dimethylnaphtalene, are included, it does not interfere.



[0016] In this invention approach, although such mixture can use a carbon number 1 thru/or five aliphatic series monocarboxylic acid, i.e., formic acid, an acetic acid, a propionic acid, butanoic acid, valerianic acid, bromoacetic acid, etc. as low-grade aliphatic carboxylic acid of a solvent, in these, an acetic acid and a propionic acid are desirable and especially an acetic acid is desirable.

[0017] The solvent used in this invention approach contains 10 - 30% of the weight of water in the above-mentioned aliphatic series monocarboxylic acid still more preferably seven to 35% of the weight preferably five to 45% of the weight. When there is less moisture in a solvent than this, the combustion loss of aliphatic series monocarboxylic acid is large, and on the contrary, if [ than this ] more, it causes the yield fall of NDCA, and a purity fall and is not desirable.

[0018] in addition, the amount of the solvent used to the dimethylnaphtalene which is a raw material, and/or its oxidation derivative -- usually -- 2 - 15 weight twice -- it is 3 - 10 weight twice preferably.

[0019] The oxidation catalyst used by this invention is the heavy metal compound and bromine compound which consist of cobalt, manganese, and a cerium. A heavy-metal oxidation catalyst is used in forms, such as organic-acid salts, such as formate, acetate, and propionate, a halogenide, a hydroxide, an oxide, and a carbonate, and is desirable. [ of a fatty-acid salt especially acetate, and a bromide ]

[0020] The sum density is 4 or less % of the weight 0.2 % of the weight or more to a solvent, and the amount of the heavy-metal oxidation catalyst used in this invention approach is 2.0 or less % of the weight 0.4 % of the weight or more preferably. It causes the yield fall of NDCA, and a purity fall and is not desirable, when there is less amount of the heavy-metal oxidation catalyst used than this or there is. [ much ] Although especially the ratio (gram atom ratio) of the manganese to cobalt is not regulated, when yield, such as ODCA, is taken into consideration, this ratio is 1.0 or less preferably. ODCA which carries out the byproduction of the addition of a cerium, and a mol -- a number -- it is -- etc. -- an amount -- or it is desirable that it is the range beyond it.

[0021] On the other hand, if it dissolves in the oxidation system of reaction and bromine ion is generated as a bromine compound, you may be any of an organic compound or an inorganic compound, and, specifically, organic bromides, such as inorganic bromides,

such as a molecule-like bromine ( $\text{Br}_2$ ), a hydrogen bromide, a sodium bromide, a potassium bromide, and an ammonium bromide, or an alkyl bromide, and a bromination fatty acid like bromoacetic acid, will be mentioned. a hydrogen bromide, a sodium bromide, a potassium bromide, a cobalt bromide, and bromination -- manganese etc. is an especially desirable example. A bromine can usually be used in 0.01-2 by the atomic ratio to the sum total of a heavy-metal oxidation catalyst.

[0022] The range of 180-230 degrees C of oxidation reaction temperature in this invention approach is 190-220 degrees C preferably. If reaction temperature is low, a reaction rate will fall, when high on the contrary, a side reaction product increases and the purity of NDCA falls. It is conditions that it is the pressure by which the system of reaction is held in reaction temperature in the first half at the liquid phase, and reaction pressure is usually 10-30kg/cm<sup>2</sup>. Extent is suitable.

[0023] As molecular oxygen content gas used in this invention approach, the mixed gas which diluted oxygen gas or it with inert gas, such as nitrogen, is used. Industrially, air is the easiest to receive and is desirable.

[0024] Although the approach of this invention is effective even if it applies it to any of a batch process oxidation style, a half-continuous system oxidation style, or a continuous system oxidation style, especially in the case of a continuous system oxidation style, it is efficient.

[0025] Rough NDCA generated by oxidation reaction can be obtained to a solid phase side by carrying out solid liquid separation of the resultant. Rough DNCA obtained according to solid liquid separation can remove an adhesion catalyst solution, oxidation reaction intermediate, and an ODCA catalyst metal complex by washing by an acetic acid etc., and backwashing by water, and high-grade-izing is possible for it. Furthermore, if the usual NDCA purification method known as a well-known approach is used when required, NDCA of a high grade can be obtained extremely.

[0026]

[Effect of the Invention] According to the approach of this invention, NDCA can be manufactured efficiently and continuously on a scale of industrial.

[0027]

[Example] Hereafter, based on an example, this invention is explained concretely. In

addition, the section and % in an example and the example of a comparison show weight section and weight %, respectively. Moreover, the cracking severity of low-grade aliphatic carboxylic acid was searched for from the gas-chromatograph analysis value of a product presentation.

[0028]

[Example 1] To the autoclave made from titanium which has the gas exhaust pipe which attached the reflux condenser, gas blowing-in tubing, a raw material continuation feeding pump, a catalytic liquid continuation feeding pump, product extraction tubing, and an agitator Acetic acid The 160 sections Cobaltous acetate and 4 monohydrate  $[\text{Co}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}]$  The 2.36 sections Manganese acetate and 4 monohydrate  $[\text{Mn}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}]$  The 1.26 sections An acetic-acid cerium and 1 monohydrate  $[\text{Ce}(\text{OOCCH}_3)_3 \cdot \text{H}_2\text{O}]$  The 3.50 sections 47% hydrogen bromide water The 0.93 sections Water The 17 sections were fed. The moisture concentration in this catalytic liquid was 10%. About this catalytic liquid, they are the temperature of 200 degrees C, and the pressure of 20kg/cm<sup>2</sup>. It is this, stirring violently under conditions. 2, 6-dimethylnaphtalene While feeding the 42 sections over 1 hour continuously, it oxidized by circulating the superfluous compressed air. Feeding of the catalytic liquid of the above-mentioned presentation was started after feeding initiation 1-hour progress of 2 and 6-dimethylnaphtalene, continuing feeding of 2 and 6-dimethylnaphtalene. Then, in order to maintain the amount of the reaction mixture in an autoclave uniformly, the reaction was continued extracting some reaction mixtures and the reaction was performed for a total of 15 hours.

[0029] The solid-state precipitation which mainly consists of NDCA was separated from the extracted reaction mixture, and the reaction mother liquor was obtained. After carrying out acetic-acid washing of the solid-state precipitation, solid liquid separation was carried out and washing filtrate was obtained. The separability of solid-state precipitation was good. At this time, the cracking severity of the yield % and the acetic acid of 3.7 mols of yield % and ODCA of 93.9 mols of NDCA was 5.0%. Moreover, all ODCA(s) contained in a reaction mother liquor and washing filtrate formed the cerium and the complex.

[0030] A reaction mother liquor and washing filtrate were condensed after whole-

quantity coalescence, and superfluous moisture was removed. At this time, it was contained in the liquid after 98.5%, 97.5%, and 6.0% condensing among the cobalt used for the reaction, manganese, and a cerium, respectively. Moreover, it was 3.7% to have been contained in the liquid after concentration among generated ODCA(s).

[0031]

[Example 2] the concentration liquid obtained in the example 1 -- washing -- the cobalt of a thing and tales doses with which it was accompanied to the cake, manganese, the cerium, and the bromine were added, an acetic acid and water were added and catalytic liquid was prepared so that the catalytic liquid used in the example 1 and catalyst concentration might become equal. The same actuation as an example 1 was performed except having used this catalytic liquid. The separability of solid-state precipitation of reaction mixture was good. At this time, the cracking severity of the yield % and the acetic acid of 3.6 mols of yield % and ODCA of 93.7 mols of NDCA was 5.2%. Moreover, all ODCA(s) contained in a reaction mother liquor and washing filtrate formed the cerium and the complex. It condensed and superfluous moisture was removed, after carrying out the whole-quantity coalescence of a reaction mother liquor and the washing filtrate. At this time, it was contained in the liquid after 97.5%, 96.0%, and 7.0% condensing among the used cobalt, manganese, and a cerium, respectively. Moreover, it was 3.5% which was contained in the liquid after concentration among ODCA(s) contained in a reaction mixture.

[0032]

[Examples 3-11] The same actuation as an example 2 was performed using the concentration liquid obtained in the example 2. The same actuation as this was repeated hereafter, and the reaction was performed a total of 10 times. The separability of the solid-state precipitation in the reaction of each time was good. Moreover, are recording of a by-product was not seen, either. A reaction result is shown in Table 1.

[0033]

[Table

1]

[0034] The most were collected at the liquid side and the great portion of ODCA has removed cobalt and manganese from the system of reaction as shown in Table 1. Moreover, since NDCA generated from the reaction intermediate dissolved in these liquid by filling up the cobalt with which it is accompanied to generation rough DNCA, manganese, a cerium, and a bromine, and carrying out the circulation reuse of a reaction mother liquor and the washing filtrate was recoverable, NDCA yield improved in the examples 2 and 3 compared with the example 1, and it turned out that level with henceforth [ good ] is maintained.

[0035]

[The example 1 of a comparison] The same actuation as an example 2 was performed except having not added a cerium in the concentration liquid obtained in the example 1. At this time, the cracking severity of the yield % and the acetic acid of 4.9 mols of yield % and ODCA of 92.0 mols of NDCA was 5.4%. At this time, 80.0% and 65.0% were contained in a reaction mother liquor and washing filtrate among the cobalt and manganese which were used for the reaction, respectively. Moreover, it was contained in the liquid after 72.0% of ODCA condensing.

[0036]

[The example 2 of a comparison] The same actuation as the example 1 of a comparison was performed using the concentration liquid obtained in the example 1 of a comparison. At this time, oxygen uptake stopped after [ of 2 and 6-dimethylnaphtalene feeding

initiation ] 40 minutes, and recovery of a reaction was impossible. In addition, the invert ratio of 2 and 6-dimethylnaphtalene was 65%.

[Claim 1] Use a dimethylnaphtalene and/or its oxidization derivative as a raw material, and even if there are few these raw materials, a twice [ 2 weight ] as many low-grade aliphatic-carboxylic-acid solvent as this is used. In the approach of using molecular oxygen content gas and oxidizing under existence of the catalyst which consists of cobalt, manganese, and a bromine (i) A chelate complex is made to form in the orthochromatic-benzene dicarboxylic acid and the selection target which added and do the byproduction of the cerium. (ii) Continuation manufacturing method of the naphthalene dicarboxylic acid which is made to remove this chelate complex out of the system of reaction, and is characterized by maintaining and carrying out the circulation reuse of the catalytic activity of cobalt (iii) and manganese.

[Claim 2] a reaction mixture -- generation after solid liquid separation -- washing which washed a cake or this with low-grade aliphatic carboxylic acid, and was obtained -- the cobalt with which it is accompanied to a cake, manganese, a cerium, and a bromine -- supplying -- a reaction mother liquor and/or generation -- the continuation manufacturing method of the naphthalene dicarboxylic acid according to claim 1 which consists of carrying out the whole-quantity circulation reuse of the washing filtrate of a cake.

[Claim 3] The continuation manufacturing method of the naphthalene dicarboxylic acid according to claim 1 whose catalyst concentration in a solvent is 0.2 % of the weight or more.

[Claim 4] The continuation manufacturing method of the naphthalene dicarboxylic acid according to claim 1 whose low-grade aliphatic carboxylic acid is an acetic acid.

[Claim 5] The continuation manufacturing method of the naphthalene dicarboxylic acid according to claim 1 which oxidizes with the reaction temperature of 180-230 degrees C.

[Claim 6] The continuation manufacturing method of the naphthalene dicarboxylic acid according to claim 1 whose moisture concentration in a solvent is 5 - 45 % of the weight.

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(54) 【発明の名称】 ナフタレンジカルボン酸の連続製造法

(57) 【要約】

【目的】 ジメチルナフタレン及び／又はその酸化誘導体を連続的に酸化せしめる改良法の提供。

【構成】 ジメチルナフタレン又はその酸化誘導体を出発原料とし、該原料の2重量倍以上の低級脂肪族カルボン酸（例酢酸）溶媒を用いて、コバルト、マンガ、臭素に更にセリウムを触媒として、分子状酸素によって酸化を行い、ナフタレンジカルボン酸を連続的に製造する方法。

【特許請求の範囲】

【請求項1】 ジメチルナフタレン及び／又はその酸化誘導体を原料とし、該原料の少なくとも2重量倍の低級脂肪族カルボン酸溶媒を用いて、コバルト、マンガン及び臭素からなる触媒の存在下に、分子状酸素含有ガスを用いて酸化する方法において、(i)セリウムを添加して副生するオルソーベンゼンジカルボン酸類と選択的にキレート錯体を形成させ、(ii)該キレート錯体を反応系外に除去せしめ、(iii)コバルト、マンガンの触媒活性を維持して循環再使用せしめることを特徴とするナフタレンジカルボン酸の連続製造法。

【請求項2】 反応混合物を固液分離後、生成ケーキ又はこれを低級脂肪族カルボン酸で洗浄して得られた洗浄ケーキに同伴されるコバルト、マンガン、セリウム及び臭素を補充して、反応母液及び／又は生成ケーキの洗浄濾液を全量循環再使用することからなる請求項1に記載のナフタレンジカルボン酸の連続製造法。

【請求項3】 溶媒中の触媒濃度が0.2重量%以上である請求項1に記載のナフタレンジカルボン酸の連続製造法。

【請求項4】 低級脂肪族カルボン酸が酢酸である請求項1に記載のナフタレンジカルボン酸の連続製造法。

【請求項5】 酸化を反応温度180～230℃で行う請求項1に記載のナフタレンジカルボン酸の連続製造法。

【請求項6】 溶媒中の水分濃度が5～45重量%である請求項1に記載のナフタレンジカルボン酸の連続製造法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、ジメチルナフタレン及び／又はその酸化誘導体を酸化してナフタレンジカルボン酸（以下、NDCAと略称することがある）を連続的に製造する方法に関するものである。更に詳しくは、酸化反応触媒を循環再使用した酸化方法に関するものである。

【0002】

【従来の技術】NDCA及びそのエステル（以下、NDCA等と略称することがある）は、高分子材料、染料中間体等として有用な物質である。特に2,6-NDCA等とエチレングリコールとから形成されるポリエチレンナフタレートはポリエチレンテレフタレートよりも耐熱性、破断強度等に優れており、フィルム、食品包装材料等の素材として注目されている。更に、ポリブチレンナフタレート樹脂はポリブチレンテレフタレート樹脂に比べて、結晶化速度が大きく、高い耐湿熱性を有しているので、NDCA等は樹脂原料としても有用である。

【0003】従来、NDCAの製造方法としては、ジア

ボン酸溶媒中、分子状酸素により酸化する方法が提案されている。

【0004】この方法は、その反応様式によって回分式、半連続式又は連続式に分類され、また、触媒を回収・再使用する場合としない場合とに分類される。

【0005】NDCAを工業的規模で安価に製造するためには、回分式又は半連続式の反応様式では装置効率が低いため、連続運転方式にして装置効率を高める必要がある。また、一般に芳香族炭化水素の液相酸化によるカルボン酸の製造では、比較的高価な触媒を使用するため、触媒を循環再使用する、即ち、反応混合物から生成粗NDCAを回収した残りの反応母液及び／又は生成粗NDCAの洗浄濾液を循環再使用することが、プロセスの経済性を高める上で有利である。

【0006】酸化反応触媒を酸化反応混合物から回収し循環再使用方法の一つとして、反応混合物から触媒のみを回収する方法が提案されている。例えば、2,6-ジイソプロピルナフタレンの酸化反応において、コバルト、マンガン、セリウム及び臭素を触媒として反応を行う際、反応母液から触媒を回収するためにアルカリを使用する方法（特開平2-250850号公報）、硫酸を使用する方法（特開平2-250851号公報）、硫酸及びアルカリを使用する方法（特開平2-252613号公報）等が提案されている。しかし、いずれの方法も、装置材質に対する腐食性、あるいは操作性という面からみて、NDCAを工業的規模で安価に製造しようとするためには、現実性、経済性ともに十分とはいえない。

【0007】一方、酸化反応触媒を酸化反応混合物から回収し循環再使用する他の一つの方法として、反応濾液を循環使用する方法が提案されている。例えば、2,6-ジイソプロピルナフタレンの酸化反応において、コバルト、マンガン、セリウム及び臭素を触媒として反応を行う際、2段反応を行って、反応濾液を循環使用する方法（特開平4-330039号公報）が提案されているが、この方法は、後酸化という工程を有しているため、プロセスの初期投資が増大し、経済性の面で有利とはいえない。

【0008】更に、2,6-ジイソプロピルナフタレン又は2,6-ジエチルナフタレンの酸化方法として、反応母液を再使用方法が提案されている（特開平4-266846号公報）。この方式による循環酸化反応は基本的には可能であるが、2,6-ジイソプロピルナフタレンや2,6-ジエチルナフタレンの酸化反応の場合、反応母液分離後の粗NDCA中には未だ多量のコバルト、マンガンを同伴されていることを考慮すると、粗NDCAを酢酸、水等で洗浄してこれらの触媒を回収して、触媒コストの低減化を図る必要がある。ところで、ジメチルナフタレンについては当該方式での酸化反応について何等言及されていない。しかも、本発明者らの検



討によると、ジメチルナフタレンの場合、当該方式で酸化反応を行うと循環初回で反応が停止してしまうという重大な問題が発生した。

【0009】本発明者らは、この原因について鋭意究明を行ったところ、2, 6-ジイソプロピルナフタレンや2, 6-ジエチルナフタレンの場合と異なって、ジメチルナフタレンの場合では循環初回で反応が停止してしまう原因は、ナフタレン核開裂副生成物であるトリメリット酸、フタル酸、メチル置換フタル酸などのオルソーベンゼンジカルボン酸類（以下、ODCAと略称することがある）が重金属酸化触媒と安定なキレート型錯体を形成して触媒を不活性化してしまうため、粗NDCAに同伴された触媒を補充するだけでは有効な触媒量が不足してしまうことによるためであることを明らかにできた。

【0010】これらの問題を回避するための方策として、多量の重金属触媒を使用するという手段が考えられるが、ジメチルナフタレンの場合（2, 6-ジイソプロピルナフタレンや2, 6-ジエチルナフタレンの場合と異なって）、収率上適正な触媒濃度が比較的低く、徒らに多量の触媒を使用すると、NDCA収率は逆に低下する。加えて生成粗NDCAが過剰に添加された重金属が酸化反応の間に変質して、生成した酸化物が変質した触媒の作用により濃灰色に着色してしまい、精製が非常に難しくなること、更に、溶媒として用いている低級脂肪酸カルボン酸の燃焼ロスが増大するという、非常に不利な結果を招く。

【0011】

【発明が解決しようとする課題】本発明は、かような状況を解消すべく、ジメチルナフタレン及び／又はその酸化誘導体からNDCAを製造するに際し、コバルトやマンガンと錯体を形成してその酸化活性を不活性化するODCAを選択的に除去して、酸化による連続製造法を提供することにある。

【0012】

【課題を解決するための手段】本発明者らは、上記方法を確立するために鋭意検討を行い、重金属及び臭素を触媒に用いたジメチルナフタレン及び／又はその酸化誘導体の液相酸化反応において、重金属酸化触媒としてコバルト、マンガンの加うるにセリウムを添加すれば、セリウムが反応系内に存在するODCAと選択的にキレート型錯体を形成し、コバルト、マンガンの酸化活性の不活性化を防ぎ、且つ固体として析出して粗NDCAに同伴されることにより、ODCAを反応母液から除去できることを見出し、本発明を完成した。

【0013】即ち、本発明は、低級脂肪酸カルボン酸溶媒中で、重金属酸化触媒及び臭素からなる触媒の存在下に、分子状酸素含有ガスを用いて、ジメチルナフタレン及び／又はその酸化誘導体を酸化する方法において、触媒を循環再使用するに際し、重金属酸化触媒としてコバルト、マンガンの加うるにセリウムを添加することによって、

コバルト、マンガンの活性を維持し、ODCAを選択的に反応系外に除去して、反応母液及び／又は生成ケーキの洗浄濾液を全量循環再使用して行うNDCAの連続製造法である。

【0014】以下、本発明を詳細に説明する。

【0015】本発明で酸化原料として用いるジメチルナフタレン及び／又はその酸化誘導体は通常どのような方法で得られたものでもよい。またそれらの混合物でもよい。酸化誘導体としては、ホルミルナフトエ酸、メチルナフトエ酸等が挙げられるが、これらには何等限定されない。そして、これらのうち、特に2, 6-体が工業的に有用である。酸化原料は高純度のものが好ましく、純度95%以上、好ましくは98%以上であるが、収率に影響を及ぼさない程度及び酸化反応終了後生成物を各種方法で精製した際除去できる程度であれば2, 6-体以外の成分、例えば2, 7-ジメチルナフタレン等の異性体を含んでいても差し支えない。

【0016】本発明方法においては、炭素数1乃至5個の脂肪酸モノカルボン酸、即ち、蟻酸、酢酸、プロピオン酸、酪酸、バレリアン酸、プロモ酢酸等、あるいはこれらの混合物が溶媒の低級脂肪酸カルボン酸として使用できるが、これらの中では酢酸、プロピオン酸が好ましく、特に酢酸が好ましい。

【0017】本発明方法において使用される溶媒は、上記脂肪酸モノカルボン酸に5~45重量%、好ましくは7~35重量%、更に好ましくは10~30重量%の水を含んだものである。溶媒中の水分がこれより少ないと脂肪酸モノカルボン酸の燃焼ロスが大きく、反対に、これより多いとNDCAの収率低下、純度低下を招き好ましくない。

【0018】なお、原料であるジメチルナフタレン及び／又はその酸化誘導体に対する溶媒の使用量は通常2~15重量倍、好ましくは3~10重量倍である。

【0019】本発明で使用する酸化触媒は、コバルト、マンガンの加うるにセリウムからなる重金属化合物及び臭素化合物である。重金属酸化触媒は蟻酸塩、酢酸塩、プロピオン酸塩等の有機酸塩、ハロゲン化物、水酸化物、酸化物、炭酸塩等の形で用いられ、脂肪酸塩、特に酢酸塩及び臭化物が好ましい。

【0020】本発明方法における重金属酸化触媒の使用量は、その合計濃度が、溶媒に対して0.2重量%以上4重量%以下であり、好ましくは0.4重量%以上2.0重量%以下である。重金属酸化触媒の使用量がこれより少ない、又は多い場合、NDCAの収率低下、純度低下を招き好ましくない。コバルトに対するマンガンの比率（グラム原子比）は特に規制されないが、ODCA等の収率を考慮すると、この比率は好ましくは1.0以下である。セリウムの添加量は副生するODCAとモル数で等量か、もしくはそれ以上の範囲であることが望ましい。

【0021】一方、臭素化合物としては、酸化反応系に溶解し、臭素イオンを発生するものであれば有機化合物又は無機化合物のいずれであってもよく、具体的には、分子状臭素( $\text{Br}_2$ )、臭化水素、臭化ナトリウム、臭化カリウム、臭化アンモニウム等の無機臭化物、又は臭化アルキル、プロモ酢酸のごとき臭素化脂肪酸等の有機臭化物が挙げられる。臭化水素、臭化ナトリウム、臭化カリウム、臭化コバルト及び臭化マンガン等が特に好ましい例である。臭素は、重金属酸化触媒の合計に対して原子比で0.01~2の範囲で通常使用できる。

【0022】本発明方法における酸化反応温度は180~230℃、好ましくは190~220℃の範囲である。反応温度が低いと反応速度が低下し、反対に高い場合は副反応生成物が増加してNDCAの純度が低下する。反応圧力は前期反応温度において反応系が液相に保持される圧力であることが条件で、通常10~30kg/cm<sup>2</sup>程度が適当である。

【0023】本発明方法において使用する分子状酸素含有ガスとしては、酸素ガス又はそれを窒素などの不活性ガスで希釈した混合ガスが使用される。工業的には空気が最も入手しやすく好ましい。

【0024】本発明の方法は回分式酸化法、半連続式酸化法又は連続式酸化法のいずれに適用しても有効である

が、特に連続式酸化法の場合に効率的である。

【0025】酸化反応によって生成した粗NDCAは反応生成物を固液分離することにより固相側に得ることができる。固液分離によって得られた粗DNCAは、酢酸等による洗浄、水洗浄によって付着触媒溶液、酸化反応中間体及びODCA触媒金属錯体を除去することができ、高純度化が可能である。更に必要な場合は、公知の方法として知られている通常のNDCA精製法を用いれば、極めて高純度のNDCAを得ることができる。

【0026】

【発明の効果】本発明の方法によれば、NDCAを工業的規模で効率よく、かつ連続的に製造することができる。

【0027】

【実施例】以下、実施例に基いて、本発明を具体的に説明する。なお、実施例及び比較例における部及び%はそれぞれ重量部及び重量%を示す。また、低級脂肪酸カルボン酸の分解率は、生成物組成のガスクロマトグラフ分析値より求めた。

【0028】

【実施例1】還流冷却器を付したガス排出管、ガス吹込管、原料連続送入ポンプ、触媒液連続送入ポンプ、生成物排出管及び攪拌機を有するチタン製オートクレーブに

酢酸	160部
酢酸コバルト・4水塩 [ $\text{Co}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ ]	2.36部
酢酸マンガン・4水塩 [ $\text{Mn}(\text{OOCCH}_3)_2 \cdot 4\text{H}_2\text{O}$ ]	1.26部
酢酸セリウム・1水塩 [ $\text{Ce}(\text{OOCCH}_3)_3 \cdot 1\text{H}_2\text{O}$ ]	3.50部
47%臭化水素水	0.93部
水	17部

を送入した。この触媒液中の水分濃度は10%であった。この触媒液を、温度200℃、圧力20kg/cm

2, 6—ジメチルナフタレン

を連続的に1時間かけて送入するとともに過剰の圧縮空気を流通して酸化反応を行った。2, 6—ジメチルナフタレンの送入開始1時間経過後、2, 6—ジメチルナフタレンの送入を継続しつつ、上記組成の触媒液の送入を開始した。その後、オートクレーブ内の反応混合物の量を一定に維持するために、反応混合物の一部を抽出しつつ反応を継続し、計15時間反応を行った。

【0029】抽出した反応混合物から主としてNDCAよりなる固体沈澱を分離して反応母液を得た。固体沈澱を、酢酸洗浄した後固液分離して洗浄濾液を得た。固体沈澱の分離性は良好であった。この時NDCAの収率93.9モル%、ODCAの収率3.7モル%、酢酸の分解率は5.0%であった。また、反応母液と洗浄濾液に含まれるODCAはすべてセリウムと錯体を形成していた。

【0030】反応母液と洗浄濾液を全量合一後、濃縮し

<sup>2</sup> の条件下で激しく攪拌しながら、これに

42部

%、97.5%、6.0%が濃縮後の液中に含まれていた。また、発生したODCAのうち、濃縮後の液中に含まれていたのは3.7%であった。

【0031】

【実施例2】実施例1で得た濃縮液に、洗浄ケーキに同伴されたものと同量のコバルト、マンガン、セリウム、臭素を添加して、実施例1で使用した触媒液と、触媒濃度が等しくなるように酢酸と水とを添加して触媒液を調製した。この触媒液を用いた以外は実施例1と同様の操作を行った。反応液の固体沈澱の分離性は良好であった。この時NDCAの収率93.7モル%、ODCAの収率3.6モル%、酢酸の分解率は5.2%であった。また、反応母液と洗浄濾液に含まれるODCAはすべてセリウムと錯体を形成していた。反応母液と洗浄濾液を全量合一した後、濃縮して過剰な水分を除去した。この時、使用したコバルト、マンガン、セリウムのうち、そ

CAのうち、濃縮後の液中に含まれていたものは3.5%であった。

【0032】

【実施例3～11】実施例2で得た濃縮液を用いて実施例2と同様の操作を行った。以下、これと同様の操作を

繰返し、計10回反応を行った。各回の反応における固体沈殿の分離性は良好であった。また、副生成物の蓄積も見られなかった。反応結果を表1に示す。

【0033】

【表1】

	収率 (モル%)		液側への分配率 (wt%)			
	NDCA	ODCA	Co	Mn	Ce	ODCA
実施例3	94.0	3.7	97.0	95.0	6.0	3.4
〃 4	94.3	3.9	96.8	96.0	5.8	3.4
〃 5	94.5	3.8	97.1	94.7	5.8	3.6
〃 6	94.5	3.6	96.9	95.1	6.6	3.3
〃 7	94.3	3.7	97.2	95.6	6.1	3.5
〃 8	94.5	3.8	97.3	94.8	6.5	3.5
〃 9	94.6	3.5	97.0	95.0	7.4	3.4
〃 10	94.5	3.6	96.7	94.7	6.2	3.2
〃 11	94.6	3.7	96.8	95.0	6.4	3.5

【0034】表1に示す通り、コバルト、マンガンは、その大部分が液側に回収され、ODCAの大部分が反応系から除去できた。また、生成粗DNCAに同伴されるコバルト、マンガン、セリウム、臭素を補充して、反応母液、洗浄濾液を循環再使用することにより、これらの液に溶解している反応中間体から生成するNDCAを回収できることから、NDCA収率は、実施例1に比べて実施例2、3で向上し、以降良好なレベルを維持していることが判った。

【0035】

【比較例1】実施例1で得た濃縮液に、セリウムを添加しなかった以外は実施例2と同様の操作を行った。この

時、NDCAの収率92.0モル%、ODCAの収率4.9モル%、酢酸の分解率は5.4%であった。この時、反応に使用したコバルト、マンガンのうち、それぞれ80.0%、65.0%が反応母液、洗浄濾液に含まれていた。また、ODCAのうち、72.0%が濃縮後の液中に含まれていた。

【0036】

【比較例2】比較例1で得た濃縮液を用いて、比較例1と同様の操作を行った。この時、2,6-ジメチルナフタレン送入開始40分間後に酸素吸収が停止し、反応の回復は不可能であった。なお、2,6-ジメチルナフタレンの転化率は65%であった。

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